SYNTHESIS AND PHOTOLUMINESCENCE STUDY OF LANTHANIDE (Dy^{3+} & Eu^{3+}) DOPED IN PHOSPHATE AND MIXED METAL OXIDES

A

PROJECT REPORT

SUBMITTED

BY

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(410CY5004)

MASTER OF SCIENCE

IN

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NATIONAL INSTITUTE OF TECHNOLOGY ROURKELA

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CERTIFICATE

This is to certify that **Mr.** Onkar Kumar Das has carried out a project entitled **'SYNTHESIS AND PHOTOLUMINESCENCE STUDY OF LANTHANIDE (Dy^{3+} & Eu^{3+}) DOPED IN PHOSPHATE AND MIXED METAL OXIDES'** under my supervision at Optoelectronics Laboratory, Department of Chemistry, National Institute of Technology, Rourkela. This work is carried out as a partial fulfilment of the award of the degree M. Sc., in chemistry of National Institute of Technology Rourkela.

04/05/2015

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DECLARATION

I hereby declare that this project report entitled **'SYNTHESIS AND PHOTOLUMINESCENCE STUDY OF LANTHANIDE (Dy^{3+} & Eu^{3+}) DOPED IN PHOSPHATE AND MIXED METAL OXIDES'** is a work carried out at Optoelectronics Laboratory, Department of Chemistry, National Institute of Technology, Rourkela under the supervision of **Dr. V. Sivakumar**, Optoelectronics Laboratory, Department of Chemistry, National Institute of Technology, Rourkela. This work contains no materials previously published or written by another person, except where acknowledgement has been made in the text.

04/05/2015

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(Onkar Kumar Das)

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Abstract

White light-emitting diodes as new solid-state light sources have a significantly capable application in the field of lighting and display. So far much effort has been devoted to exploring novel luminescent materials for White LEDs. Currently the major challenges in WLEDs are to achieve high luminous efficacy, high chromatic stability, brilliant color-rending properties, and price affordability against fluorescent lamps, which depend on critically on the phosphor properties. Numerous efforts have been made to develop single-phase white-light-emitting phosphors. In the present study, the Dy^{3+} doped phosphates have been synthesized and optical studies have been carried out. The Dy^{3+} doped compositions show wide range of color in the visible region (organish-yellow to white). In addition, efforts also been made to synthesis Eu^{3+} substituted mixed metal oxides ($La_{0.95}Eu_{0.05}BW_{1-x}Mo_xO_6$ (x = 0 – 1) and studied their photoluminescence properties. Selected compositions show good red emission under near UV to blue ray excitation. The presently studied compositions may find potential application as yellow and red phosphor for white LEDs.

1. INTRODUCTION:

The rare earth elements have a unique and important impact on our lives. The unfilled 4f electronic structure of the rare earth elements makes them have special properties in luminescence, magnetism and electronics, which could be used to develop many new materials for various applications such as phosphors, magnetic materials, hydrogen storage materials and catalysts [1]. Solid-state lighting technology has now already penetrated in a variety of specialty applications, in result, LEDs have completely changed the "world of luminance", for example automobile brake lights, traffic signals, liquid crystal displays and mobile backlights, flashlights and all manner of architectural spotlights [2]. In specific, the invention of high-efficiency blue-emitting InGaN-based LEDs makes understanding of efficient, full-spectrum white-light LEDs for general illumination possible by using conversion phosphors, and will bring about a revolution in lighting industry [3].

The history of lighting can be observed as the development of increasingly efficient technologies for generating visible light inside, but not wasted light outside, of that spectral region. There are three types of traditional technologies and they are Incandescence, Fluorescence, and High Intensity Discharges (HID). These three traditional technologies are made significant progress over the past 200 years, but performing at efficiencies in the 1-25% range. A new, fourth technology is Solid-State Lighting. In this principle, a forward biased electrons and holes of semiconductor are recombine and producing photons; the resultant photon are observed from the chip. Then these photons are either mixed with different-color photons from the LEDs, or phosphor materials which are producing different color. By choosing different colored phosphors and finally create white color. The use of rare-earth element-based phosphors, based on line-type f–f transitions, can narrow emissions to the visible range, resulting in high efficiency and high lumen equivalence. Rare-earth Dy^{3+} ions have two dominant emission bands, one in the blue region (470–500 nm) and one in the yellow region (560–600 nm). The two emissions originate from $^4F_{9/2} \rightarrow {}^6H_{13/2}$ and $^4F_{9/2} \rightarrow {}^6H_{15/2}$ transitions of Dy^{3+} ions, respectively. The yellow emission of Dy^{3+} is especially hypersensitive to the local environment, whereas the blue emission is not. Therefore, by suitably adjusting the yellow-to-blue intensity ratio, it is possible to obtain a phosphor with near-white-light emission. It is the candidate for the potential white light emission phosphor with a single emitting center for luminescent materials doped with Dy^{3+} ions [5,6].

1.1 Phosphor:

Luminescent materials, also known as phosphors, the term phosphor means “light bearer”. In general, a phosphor is a solid that converts certain types of energy into electromagnetic radiation over and above the thermal radiation [6]. In order to get the desired wavelength (color), phosphors are synthesized doping with transitional ions like Mn, Bi and rare earths like Eu, Tb, Ce etc. the practical size of the phosphors is critical in the development of various phosphors for different applications.The emissions usually fall into the visible region but also could be invisible, such as ultraviolet [13] or infrared light [1, 14]. The phosphors materials that are used in the fluorescent lamp are primarily convert the UV emission of the rare gas/ mercury discharge plasma into white radiation. To meet the demands for various applications, phosphors are usually in the form of powders with specific requirements on particle size distribution and morphology [15]. Usually, larger crystals (4 to 5 μm) of high quality are required [16] since the quantum efficiencies are generally higher in crystals than in amorphous hosts [17]. There are so many phosphor materials are discovered but many of potential phosphor candidates are ruled out due to their direct contact with mercury discharge. For example, sulphide phosphors (Zns) cannot be used, since they react with Hg. Therefore oxides are used as the hosts for these applications. Subsequently a main aim of lamp phosphor development is to achieve a strong absorption of the mercury emission followed by an effective conversion into visible light. In earlier they produced halo-phosphate lamps. As much as the development of phosphor is concerned, Eu^{2+} ion was frequently used as an activator ion in various host lattices. Due to the shielding effect of the outer shells, the 5d electrons split easily by the crystal field around it. Thus the peak position of Eu^{2+} emission strongly depends on the Eu^{2+} ions surrounding, consequently, Eu^{2+} ions can emit from near UV to red region of the spectrum.

1.2 Luminescence:

Luminescence is an emission of light it comes when the de-excitation of electron from the excited state to ground state i.e. when an electromagnetic radiation is applied to solid or gaseous materials, excites the molecules and the substance glows. There are different types of luminescence and the same have been categorized based on their excitation source (Table 1). For example, if the chemical reaction energy is the excitation source then the observed luminescence is called chemiluminescence.

Table. 1. Types of luminescence and examples

S.No.	Type of luminescence	Excitation source	Example
1	Bioluminescence	Bio-chemical energy	firefly, Photinuspyralis
2	Cathodoluminescence	Cathode rays (high energy electrons)	microscope
3	Chemiluminescence	Chemical reaction energy	luminol + hydrogen peroxide → 3-aminophthalate+ light
4	Electroluminescence	Applied voltage	OLEDs
5	Photoluminescence	Photons (UV, Visible)	
6	Radioluminescence	X-rays, γ rays, etc.	Radium salt
7	Sonoluminescence	Sound waves	Bubbles in liquid
8	Thermoluminescence	Thermal stimulation of emission, which is excited by some other means.	Sediment grains
9	Triboluminescence	Mechanical energy such as grinding, stress, etc.	Diamond

Host/self-sensitized luminescence

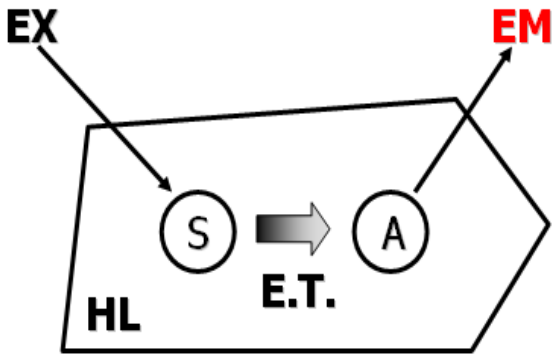

Fig. 1. Schematic diagram of luminescence mechanism

Sensitizer sensitized luminescence: sensitizers also play an important role in the luminescent materials, and can absorb the excitation energy and transfer it to the activators. So, the luminescent properties are improved or enhanced greatly [7]. We define these luminescent materials as ‘‘host + sensitizer + activator’’ type. For example, the Ce^{3+} ion is a good sensitizer for the Tb^{3+} ion in the $LaPO_4:Ce^{3+}$, Tb^{3+} phosphor, and can transfer its excitation energy to Tb^{3+} and make the latter display green emission.

Activator luminescence: Most luminescent materials consist of inactive host and luminescent ions (i.e. activators as luminescent centers). For example, Y2O3 as a host material cannot luminesce directly. When Eu3+ ions are doped into Y2O3, it can emit red light. So we define these luminescent materials as ‘‘host + activator’’ type.

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Activator luminescence: Most luminescent materials consist of inactive host and luminescent ions (i.e. activators as luminescent centers). For example, Y_2O_3 as a host material cannot luminesce directly. When Eu^{3+} ions are doped into Y_2O_3, it can emit red light. So we define these luminescent materials as ‘‘host + activator’’ type.

1.3 Lanthanide Luminescence

The alkali earth aluminates containing rare earth ions are functional inorganic materials used for the synthesis the blue and red emitting phosphor materials [8-10]. These materials are generally used for such devices “glow-in-dark” objects as, direction indicators, safe helmets and signs, varieties of toys, robber shoe soles and the like due to their better safe, excellent photo resistance, chemical stability, very bright and long lasting afterglow with no radio-active radiations and hence forms the important materials in various ceramics industries [11].

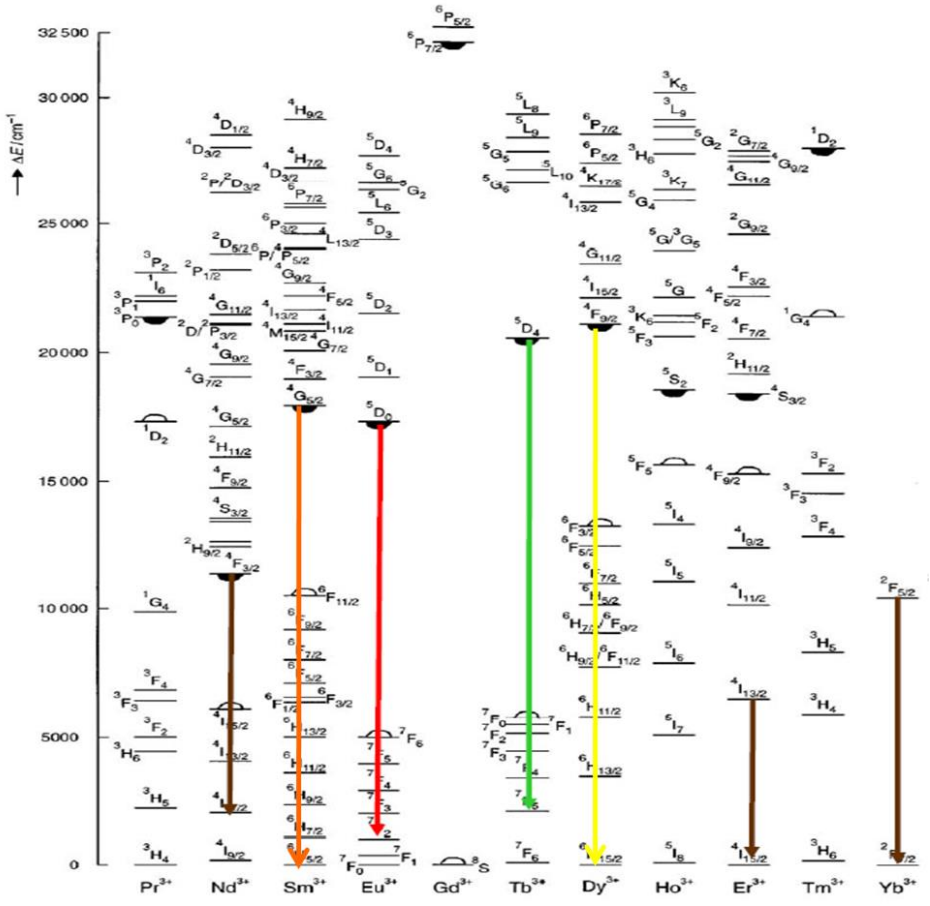
In recent years, $SrAl_2O_4$ and $Sr_4Al_{14}O_{25}$ phosphors doped with Eu^{2+} and Dy^{3+} ions have been regarded as outstanding phosphors and attracted the scientist’s interest [12-13]. For the improvement of phosphorescent properties, research has been focused on concerning extracts, molar ratio of constituents and the planning methods [11-12]. Z. Wu et al. reported the control of particle size by adopting the sol-gel and co-precipitation methods [13]. It was found that the shape and size of phosphor particles plays important role for the fluorescence properties of $Sr_4Al_{14}O_{25}:Eu^{2+}$ phosphor. When the particle size reaches the nano scale, new properties are appeared like the blue shift of emission intensity [14]. If the phosphor particles are flat plate, then they are expected to give a better light absorption and form a thick close solid by their orientation, resulting higher photoluminescence intensity.

Phosphor of smaller particles size can be synthesized by the liquid phase reaction methods like sol-gel [15-16], co-precipitation [17] microwave [18] and combustion [19] synthesis methods. In the liquid phase synthesis methods, each constituent (especially, activator ions) can be exactly controlled and equally dispersed throughout the phosphor materials, which is of major importance for the phosphor properties. Additional, the liquid phase synthesis methods like sol-gel, chemical combustion, and chemical co-precipitation methods are often used as low temperature paths to combine the activator ions into the phosphor host lattices. By using of surfactants and capping agents like glycerol etc. can support in the exact control of a chemical reaction and hence the morphology of the phosphor particles.

The color which is produced from halo-phosphate lamp is not ideal and it is necessary to produce higher CRI. The first report of a fluorescent lamp based on new concept was made by Haft and Thornton in 1972. The phosphor combination of $3Sr_3(PO_4)_2.SrCl_2:Eu^{2+}$, $Zn_2SiO_4:Mn^{2+}$ and $Y_2O_3:Eu^{2+}$ (blue, green, and red) with color temperature 4200 K, however this concept not been commercialized due to the reliability poor maintenance characteristics of the phosphors [7].

Eu ion activated phosphors emit bright red light. Eu^{3+} has been incorporated into many host lattices, such as YVO_4 [18], Y_2O_2S, Y_2O_3 to develop red light emitting phosphors for cathode-ray televisions (CRTs). Eu^{3+} has also been investigated for X-ray detection [20]. Eu^{3+} ions usually occupy the sites that have no inversion symmetry in the host crystals. The strong red emission line at around 610 to 630 nm is due to the electric dipole transition of $^5D_0 \rightarrow {}^7F_2$. Eu^{3+} ions can also occupy the sites of inversion symmetry, as in $InBO_3$ [20]. If it occurs the emission line at ~ 600 nm due to the magnetic dipole transition of $^5D_0 \rightarrow {}^7F_1$ becomes relatively stronger and dominates.

$YVO_4:Eu^{3+}$ was developed in 1964 [18] to meet the demands for an appropriate red phosphor for use in colour TV. This was later replaced by $Y_2O_2S:Eu^{3+}$ for better energy efficiency [20] and stability in the recycling in the screening process of CRT production. $Y_2O_3:Eu^{3+}$ has been used for a high colour rendering lamp as well as for FED displays [20]. The classic Dieke diagram of lanthanide ions is shown in Fig. 1. It explains the energy levels of lanthanides and their corresponding emitting levels.



Classic dieke diagram

1.4 Solid state lighting Literature survey:

Numerous Eu^{2+} substituted phosphate phosphors, such as $Ba_2Mg(PO_4)_2$, [21] $Ca_{10}K(PO_4)_7$, [22] Ca_2PO_4Cl, [23] $Sr_6BP_5O_{20}$, [24] $Ba_5(PO_4)_3Cl$, [25]. $Ca_5(PO_4)_3Cl$, [26] $M_5(PO_4)_3Cl$ (M = Ca, Sr, Ba), [27] $KSrPO_4$,[28] $Sr_8Mg(Y,La)(PO_4)_7$, [29] $LiBaPO_4$, [30] and $Sr_2P_2O_7$, [31] have been studied for white LEDs because they have moderate synthesis temperatures and good physical and chemical stabilities. Recently, many researchers have studied the phosphate host lattice with whitlockite-type structure for white light emitting phosphor such as, Ca9Lu(PO4)7:Eu^{2+},Mn^{2+}, [32]. $Ca_8MgGd(PO_4)_7$:Eu^{2+}, [33] $Ca_8MgR(PO_4)_7$:Eu^{3+} (R= La, Gd, Y), $Sr_8ZnSc(PO_4)_7$:Eu^{2+} [34] have been reported for LED phosphors due to their outstanding luminescence properties as down-conversion phosphors. However, as far as we know, standard white with CIE color coordinate of (0.33, 0.33) is still unrealized in whitlockite-type phosphors, for instance, (0.353, 0.324) in $Ca_9La(PO_4)_7$:Eu^{2+},Mn^{2+} [35].and (0.333, 0.268) in $Ca_9Lu(PO_4)_7$:Eu^{2+},Mn^{2+}.[36]. D. Geng et al., has studied the Color-Tunable and White Luminescence Properties via Energy Transfer in Single-Phase $KNaCa_2(PO_4)_2$:A (A = Ce^{3+}, Eu^{2+}, Tb^{3+}, Mn^{2+}, Sm^{3+}). [37].

1.5 Motivation for the present study:

To understand the lanthanide luminescence in $Sr_{1.75}Ca_{1.25}(PO_4)_2$ and create yellow and white light emission in Dy^{3+} doped phosphates. Further we also synthesised novel red emitting phosphor based on mixed metal, oxides ($La_{0.95}BW_{(1-x)}Mo_xO_6 : 0.05Eu^{3+}$) and their respective properties. The main objective of present investigation is to find a better host lattice for Dy^{3+} and to obtain yellow/white phosphor. Efforts also made to investigate the Eu^{3+} luminescence in $La_{0.95}BW_{1-x}Mo_xO_6$ solid solution, in order to understand structure- property- correlation in the mixed metal oxides. The concentration of Dy^{3+} has been varied to fine tune the emission ranging yellow to white in the host lattice $Sr_{1.75}Ca_{1.25}(PO_4)_2$. The mechanism of luminescence and electronic transition during luminescence has also been discussed in details.

2. EXPERIMENTAL SECTION

2.1 Materials

The high-purity (99.99%) compounds were used as precursor and it was a mixture of reagent grade $CaCO_3$ (Merck), $(NH_4)_2HPO_4$ (Merck), Na_2CO_3 (Alfa), Dy_2O_3 (Alfa), La_2O_3 (Alfa), Eu_2O_3 (Alfa), H_3BO_4 (Merck), WO_3 (Alfa), MoO_3 (Alfa).

2.2 Synthesis of $La_{0.95}Eu_{0.05}BW_{1-x}Mo_xO_6$

The Eu^{3+} doped host lattice $La_{0.95}Eu_{0.05}BW_{1-x}Mo_xO_6$ was synthesized by conventional high temperature solid-state reaction. The doping concentration of Eu^{3+} is from 0 to 1.0 mol % insteps of 0.2. The corresponding precursors are weighed according to the stoichiometric ratio. Each mixture of starting materials is ground for an hour, loaded into a high purity silica crucible, and then sintered using furnace. First, the stoichiometric mixture was slowly heated up to 600°C for a duration of 3 hours and was kept at this temperature for 6 hours. The obtained powder was mixed again and then heated up to 1000 °C for a duration of 4 hours and was kept at this temperature for 12 hours. The sample was then thoroughly mixed and cooled down to room temperature to obtain white powder. This synthesis was carried at normal ambient. The obtained synthesized powder is characterized for its structural and optical properties.

2.3 Synthesis of $Sr_{1.75}Ca_{(1.25-2x)}(PO_4)_2:xDy^{3+},Na^+$ (x = 0−0.15) by solid state method:

The $Sr_{1.75}Ca_{(1.25-2x)}(PO_4)_2:xDy^{3+},Na^+$ (x = 0−0.15) powder samples were synthesized by the high temperature solid-state reaction method. The starting materials, $SrCO_3$ (A.R. grade), $CaCO_3$ (A.R. grade), $(NH_4)_2HPO_4$ (A.R. grade), Na_2CO_3 (alfa), Dy_2O_3 (alfa), Sm_2O_3 (alfa)

and Eu_2O_3 (99.99% purity), were stoichiometrically weighed and thoroughly mixed by an agate mortar and pestle. First, the mixtures were preheated at 700 °C for 2 h in a muff furnace in air to release NH_3, CO_2, and H_2O. Then, the precursor was reground and heated at 1250°C for 5 h in a tube furnace in air atmosphere. Finally, the samples were furnace-cooled to room temperature with cooling rate of ∼10 °C/min.

2.4 Preparation of $Sr_{1.75}Ca_{(1.25-2x)}(PO_4)_2:xDy^{3+},Na^+$ (x = 0−0.15) by Co-precipitation Method: The $Sr_{1.75}Ca_{(1.25-2x)}(PO_4)_2:xDy^{3+},Na^+$ (x = 0−0.15) powder sample were synthesized by co-precipitation method. The starting material $(NH_4)_2HPO_4$ (A.R. grade) weighed and dissolved in distilled water and make anion solution named as solution A. The starting materials, $SrCO_3$ (A.R. grade), $CaCO_3$ (A.R. grade), Na_2CO_3 (merck), Dy_2O_3 (alfa), Sm_2O_3 (alfa) and Eu_2O_3 (99.99% purity), were weighed and dissolve in conc. HNO_3 to make cation solution named as solution B. The anion solution A is taken in round bottom flask. The cation solution B is slowly pour into the round bottom flask containing anion solution. The mixture of both solution put onto the magnetic stirrer and stir for 3 hours and get precipitate. The solution was evaporated and put into the oven whole night to get solid precipitate. Then the precipitate was grounded and divide into two half. One half precipitate taken into crucible and put into muffle furnace to heat 1000°C for 2 hours. Other half precipitate taken into other crucible and put into muffle furnace to heat 1100°C for 2 hours. Finally furnace were cooled to get the samples.

2.5 Characterisation

The Phase purity was checked by powder X-ray diffraction (XRD) analysis collected on a RIGAKU JAPAN/ULTIMA-IV Diffract meter using Ni-filtered Cu Kα radiation (λ = 1.5406 Å). The Photoluminescence - PL and PLE spectra were recorded on a Fluoromax-4P Spectroflurometer [Horiba Jobin Yvon] equipped with a 150 W Xe lamp as the excitation source. Diffuse Reflectance Spectra is measured with Shimadzu Spectrophotometer (UV-2250) in the range of 200 – 800 nm. The colour chromaticity coordinates was calculated from emission data. All the measurements were observed at room temperature.

3. RESULTS AND DISCUSSION

3.1 Phase Formation and Structural Analysis

The crystal structure $LaBMO_6$ [M = W/Mo] is shown in Fig.1. In order to find the phase formation and structure of the synthesized phosphor material, the Powder X-ray diffraction

(PXRD) is done. Figure – 1 shows the XRD patterns of the synthesized compound at room temperature. All the reflections are well matched and good in agreement with JCPDS card no. 35-0261 (ICDD) International Centre for Diffraction for Database. From XRD, it is clear that well matches with two phases, ie., for the compositions $LaBWO_6$ its well matched with JCPDS card No. 37-1100. The unit cell parameters are *a* = 0.410 A°, *b* =1.031 A°, *c* =2.171 A°, and the interfacial angle β = 98.108, space group = P_{22}, and the remaining composition well indexed to another JCPDS card No. 37-1100. The unit cell parameters are *a* =10.2863 A°, *b* =4.15790 A°, *c* =16.3390 A° and the interfacial angle beta = 98.830 A°, Z = 6 space group = P21, volume= 690.53 A° ^{3}. The typical XRD patterns of Eu^{3+} (x = 0.05) doped, mixed oxide of $LaBWO_6$ and $LaBMoO_6$ compounds were shown in Fig. 1. All the diffraction peaks in the XRD patterns of the samples could be indexed to the standard card of JCPDS No.35-0261 for LaBWO6 and JCPDS No. 37-1100 for $LaBMoO_6$. The dopant Eu^{3+} doesn't change the structure of the synthesized compound, due to the similarity in the ionic radii. The ionic radii of Eu^{3+} is 9.47 nm. One can observer there is a phase transition occurs in the composition $La_{0.95}Eu_{0.05}BW_{0.6}Mo_{0.4}O_6$ to $La_{0.95}Eu_{0.05}BW_{0.6}Mo_{0.4}O_6$.

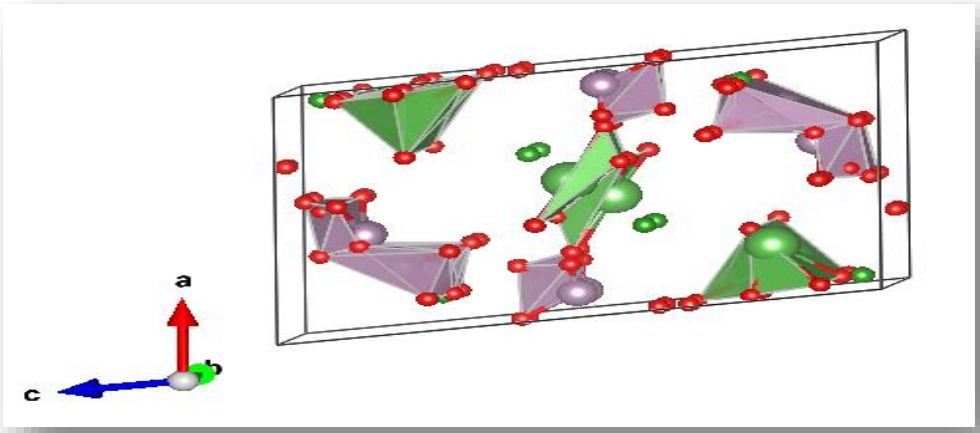


Fig.1. The crystal structure $LaBMO_6$ [M = W/Mo]

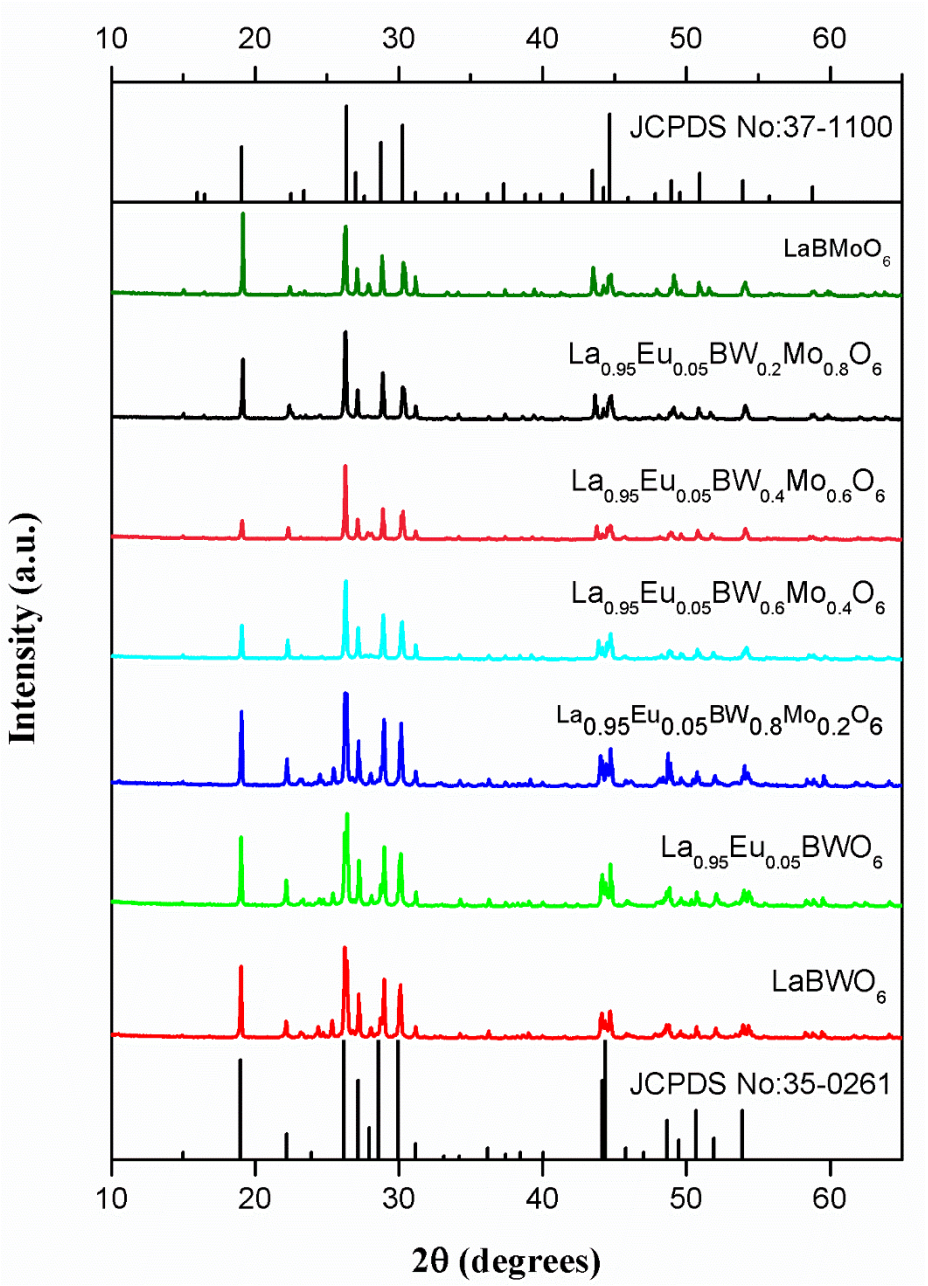


Fig 2. XRD patterns of $LaBWO_6$, $La_{0.95}BW_{(1-x)}Mo_xO_6$:0.05$Eu^{3+}$ incorporated with different ratio of Mo and W, $LaBMoO_6$ phosphors and JCPDS card related to this phosphor (35-0261) and (37-1100).

3.2 Diffuse Reflectance Spectroscopy (DRS):

Fig 3 shows the absorption spectra of compounds synthesized. It shows that all the compounds are absorbing in the UV region (200 to 400 nm). There is a strong absorption in the visible region i.e. from 200 to 370nm due to the host. Sharp breakdown from 370nm to 400nm which is due to the activator Eu^{3+} (f-f transition).Broad absorption band is observed

for all compositions and this band is due to charge transfer transition from O → W. In other words electronic transition from valence band (primarily oxygen 2p non-bonding character) to conduction band (arises from p* interaction between the tungsten metal ion t_{2g} orbital and oxygen). From the DRS spectra the bad gap of $La_{0.95}BW_{1-x}Mo_xO_6$ is found to be 3.6 eV shown in the fig 3.3e and remaining all band gap values shown in Table-1.

Absorbance

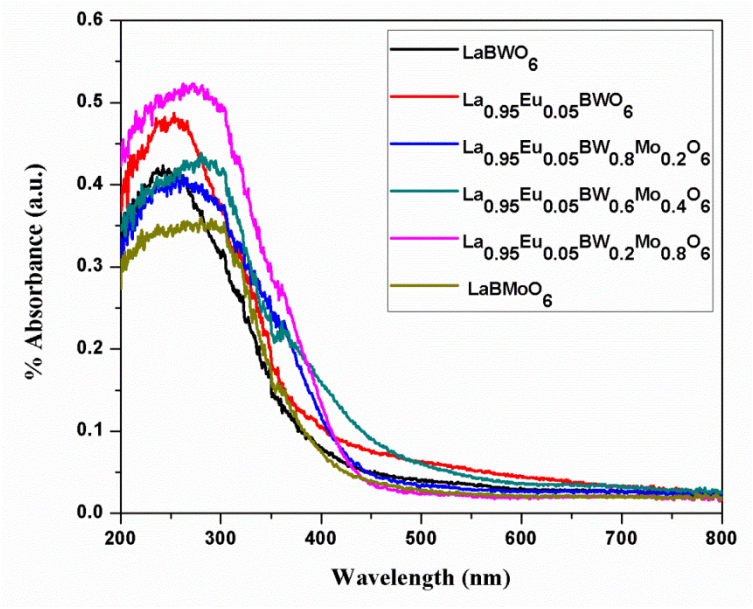


Fig 3. UV−vis absorption spectra of $La_{0.95}BW_{(1-x)}Mo_xO_6$:0.05$Eu^{3+}$

Reflectance:

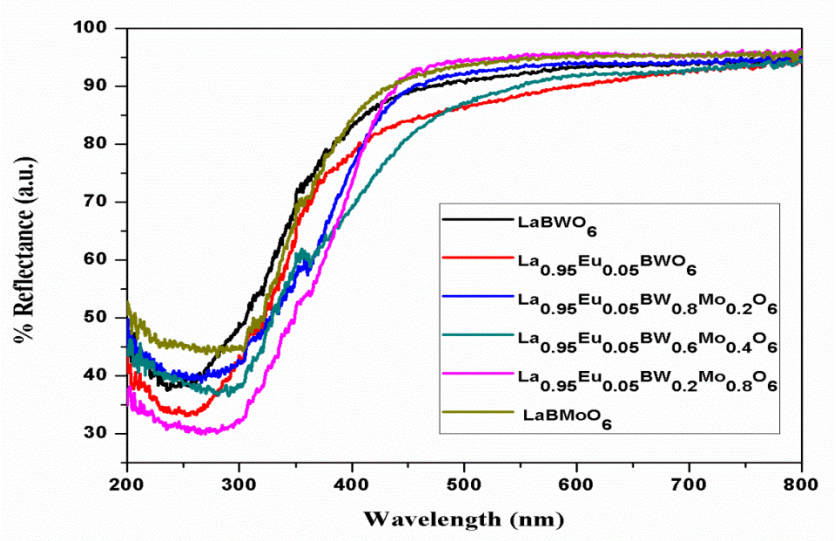


Fig 4. UV−vis reflectance spectra of $La_{0.95}BW_{(1-x)}Mo_xO_6$:0.05$Eu^{3+}$

3.3 Band Gap:

Reflectance and Band gap for W

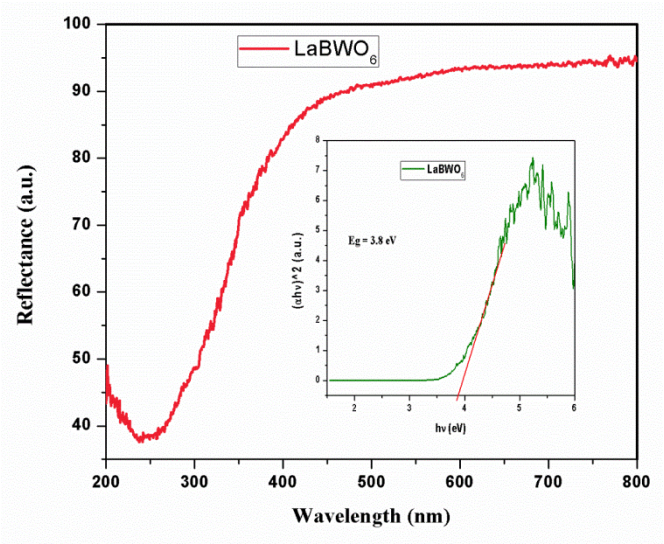


Figure 5. Calculated energy gap (Eg) and DRS spectra of $LaBWO_6$.

Reflection and band gap for Mo

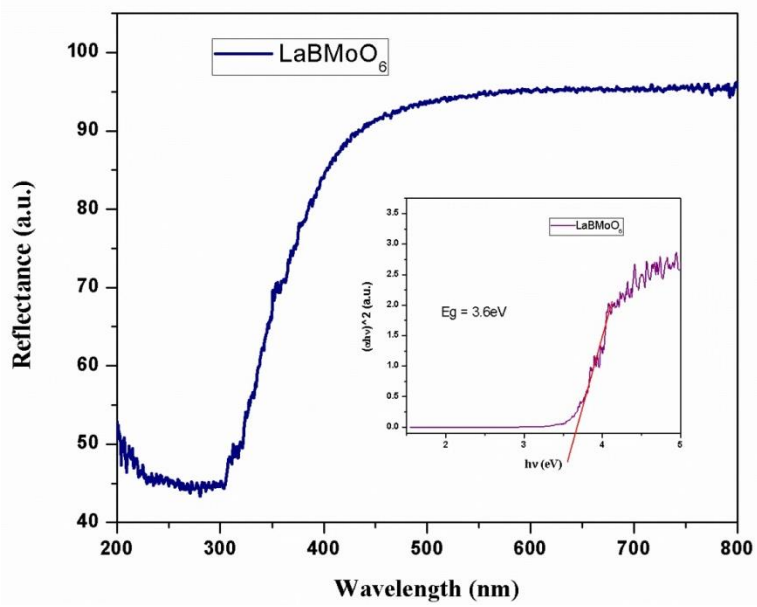


Fig 6. Calculated band gap (Eg) and DRS spectra of $LaBMoO_6$

Table1. Band Gap values of synthesized compounds.

Composition	Band Gap (eV)
$LaBWO_6$	0.380
$La_{0.95}Eu_{0.05}BWO_6$	0.382
$La_{0.95}Eu_{0.05}BW_{0.8}Mo_{0.2}O_6$	0.384
$La_{0.95}Eu_{0.05}BW_{0.6}Mo_{0.4}O_6$	0.373
$La_{0.95}Eu_{0.05}BW_{0.4}Mo_{0.6}O_6$	0.374
$La_{0.95}Eu_{0.05}BW_{0.2}Mo_{0.8}O_6$	0.362
$LaBMoO_6$	0.360

3.4 Photoluminescence Spectroscopy (PL)

Fig. 7. Show the typical luminescence spectra of Eu^{3+} ion when excited under (393/465 nm). The corresponding emission spectrum consist of 3 major emission which appear at 596, 615 and 650 nm respectively.

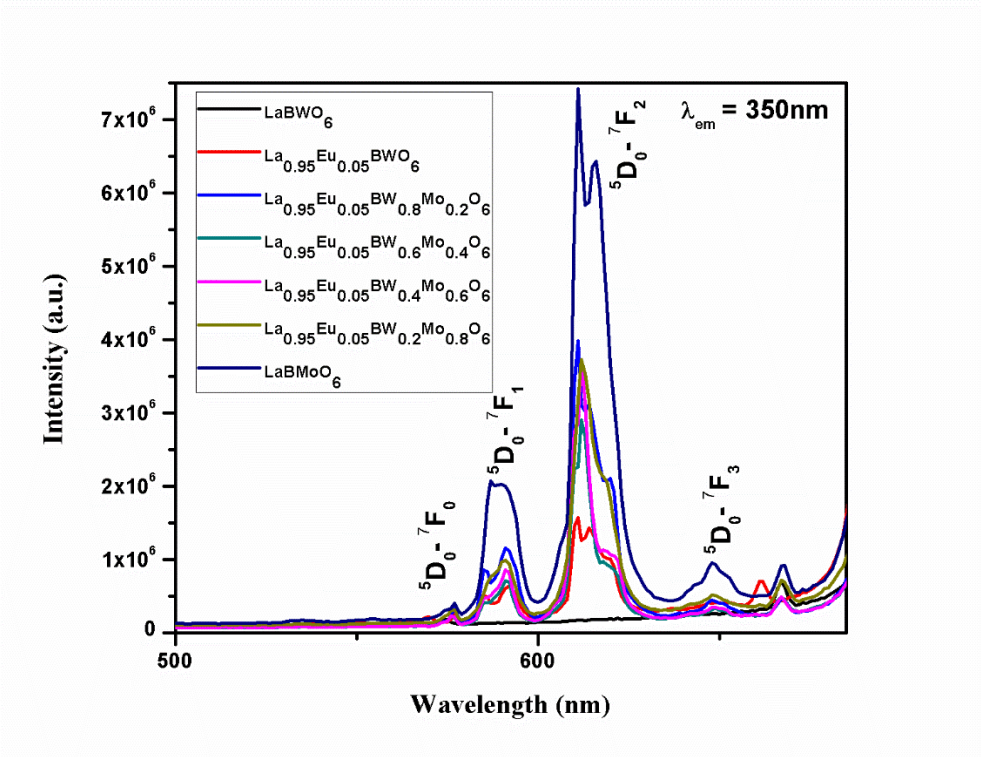


Fig. 7. Emission intensity dependence on Eu^{3+} concentration of $La_{0.95}BW_{(1-x)}Mo_xO_6$:0.05$Eu^{3+}$ phosphors (λ_{ex} = 350 nm).

$^5D_0 - {}^7F_1$ (magnetic dipole), $^5D_0 - {}^7F_2$ (electrical dipole), $^5D_0 - {}^7F_3$ dominating transmission which provide information that Eu^{3+} occupied site of inverse symmetry. This attributed due to electric dipole transition at 615 nm. We get intense red emission due to

$^5D_0 - {}^7F_1$ transition whereas the $^5D_0 - {}^7F_1$ also a major transition of Eu^{3+}, it is attributed as magnetic dipole transition gives a mixed orangish red emission near about 596 nm. The emission intensity depend upon the good absorption capacity of host lattice. The broader absorption of host from 250-400 nm under UV gives a sharp line like emission, which is fulfilled by the phosphor synthesized by broad CT band absorbed from UV due to O-W or O-Mo charge transfer. It transfer all its energy to the Eu^{3+} (central metal ion) which give a line like emission at 615 nm.

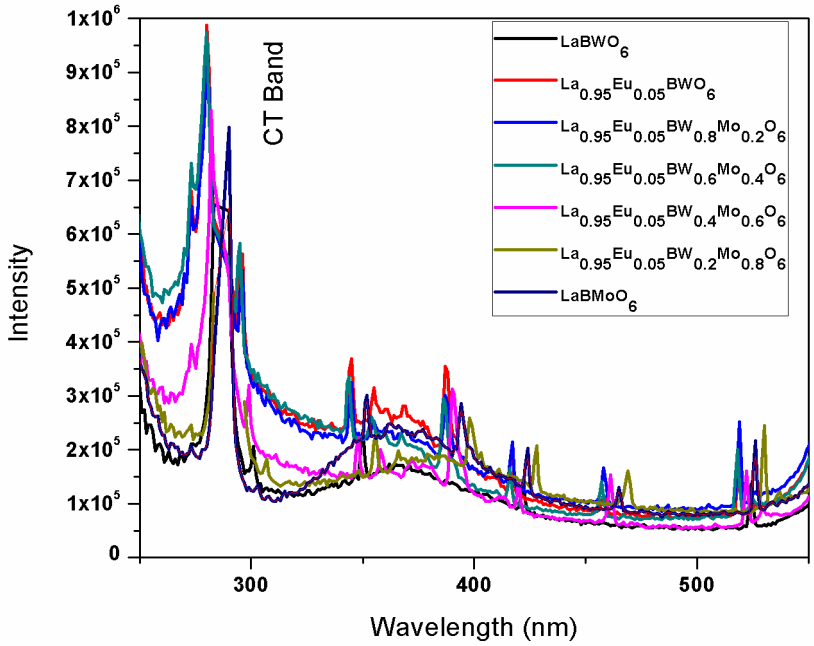


Fig 8. PL excitation of $La_{0.95}BW_{(1-x)}Mo_xO_6$:0.05$Eu^{3+}$

3.5 Commission International del'Eclairage (CIE) chromaticity coordinates

The CIE (Commission International del'Eclairage - 1931) chromaticity coordinate values of emissions for the doped compounds are calculated and is indicated by a Fig3.5a, the inset shows the photographs of doped samples taken under UV light (excited at 365 nm). The CIE values for the various concentrations are summarized in the Table-2.

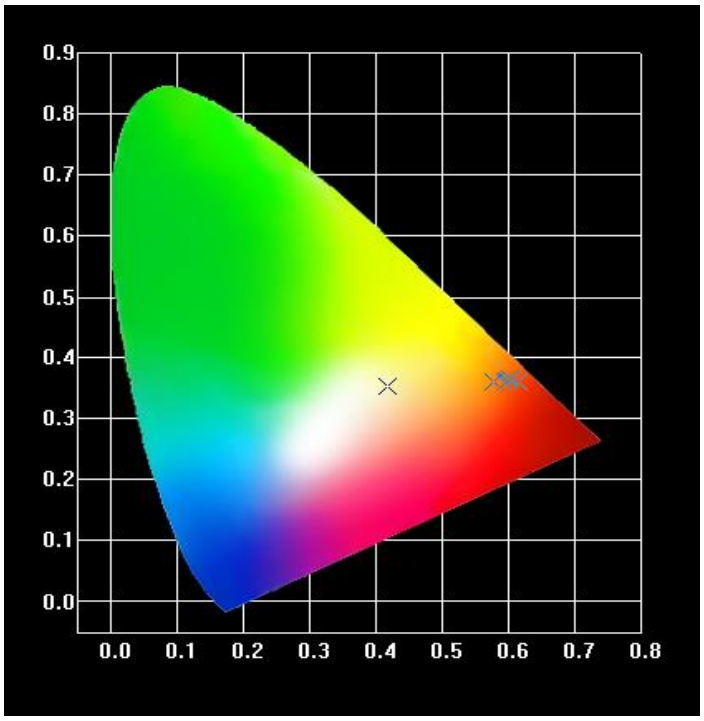


Fig 9. CIE of $La_{0.95}BW_{1-x}Mo_xO_6:0.05Eu^{3+}$

The intense emission from the activator Eu^{3+} ions results in red colour with the CIE chromaticity coordinate values x = 0.6647 and y = 0.3349, which were close to the National Television Standard Committee (NTSC) standard values with (x = 0.670 and y = 0.330). Hence, this red phosphor can find potential applications in the white LED based on yellow + red phosphor.

Table-2 CIE values of synthesized compounds.

Composition	X	Y
$LaBWO_6$	0.4177	0.3529
$La_{0.95}Eu_{0.05}BWO_6$	0.6031	0.3657
$La_{0.95}Eu_{0.05}BW_{0.8}Mo_{0.2}O_6$	0.5973	0.3635
$La_{0.95}Eu_{0.05}BW_{0.6}Mo_{0.4}O_6$	0.6151	0.3612

$La_{0.95}Eu_{0.05}BW_{0.4}Mo_{0.6}O_6$	0.6101	0.3602
$La_{0.95}Eu_{0.05}BW_{0.2}Mo_{0.8}O_6$	0.5940	0.3612
$LaBMoO_6$	0.5768	0.3596

3.6 Digital photograph of $LaBWO_6$ and Eu^{3+} Doped $LaBWO_6$

Host compound i.e. $LaBWO_6$ under UV 365nm shows no color as shown in Fig 10. but Eu-doped compound shows intense red color under UV 365nm as shown in Fig 10. which indicates the presence of Eu in the host lattice.

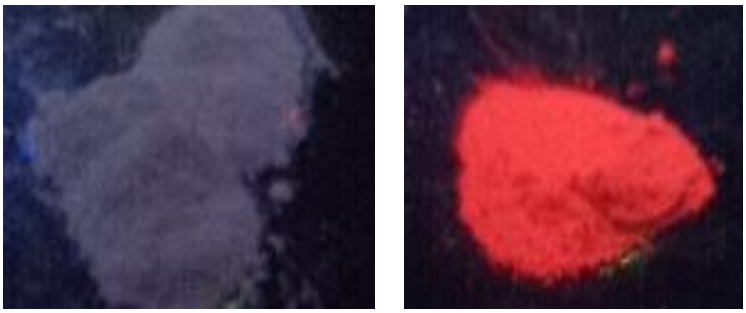


Fig 10. The digital photograph of $LaBWO_6$ and $LaBWO_6$:Eu^{3+}under UV 365 nm

3.7 Crystal Structure and XRD study of $Sr_{1.75}Ca_{1.25}(PO_4)_2$

$Sr_{1.75}Ca_{1.25}(PO_4)_2$ is isostructural to β-$Ca_3(PO4)_2$ structure, which crystallizes in the space group R3c [38]. In a typical whitlockite structure compound like β-$Ca_3(PO_4)_2$, the Ca^{2+} cations occupy five positions and one vacancy; Ca1 and Ca2 are eight-coordinated, Ca3 is nine-coordinated by oxygen atoms, the distorted octahedral (six-coordinated) Ca5 site is fully occupied, Ca4 is surrounded by nine oxygen atoms and half-occupied by calcium cations, and Ca6 is a vacancy. The Sr/Ca sites in the $Sr_{1.75}Ca_{1.25}(PO_4)_2$ structure correspond to the (Ca1, Ca2), Ca3, (Ca4, Ca6), and Ca5 sites in the β-$Ca_3(PO_4)_2$-type structure, respectively. The powered XRD patterns of synthesized compounds $Sr_{1.75}Ca_{1.25}(PO_4)_2$ doped with various Dy^{3+} ion concentration are shown in fig. 6 -10. All the compositions show single phase formation and no impurity lines were identified.

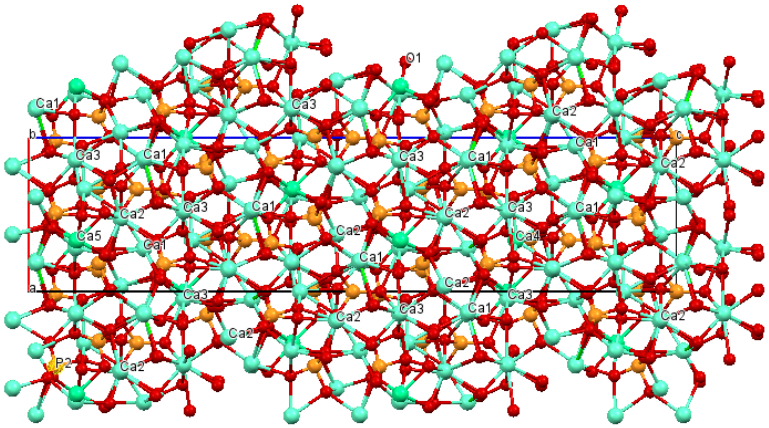


Fig 4. The crystal structure of $Sr_{1.75}Ca_{1.25}(PO_4)_2$

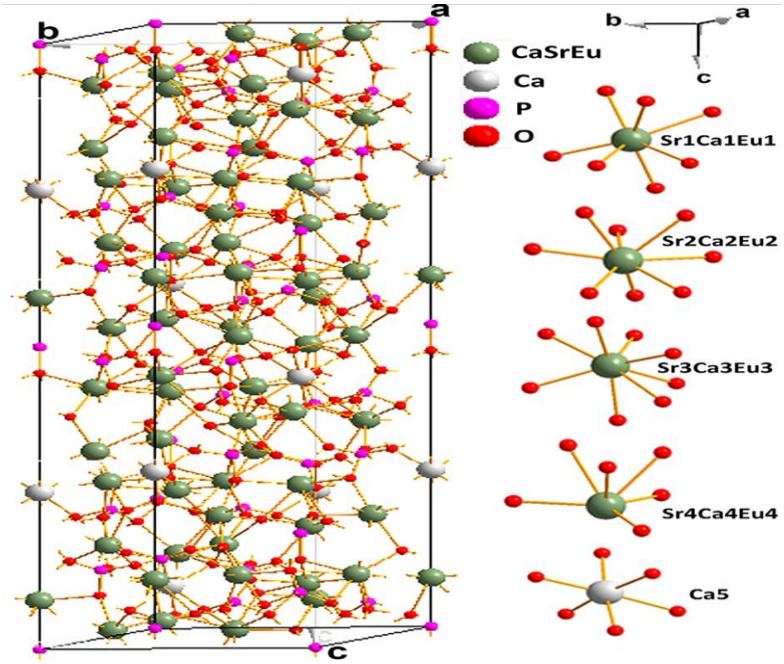


Fig 5. The crystal structure of $Sr_{1.75}Ca_{1.25}(PO_4)_2$ with coordination sites

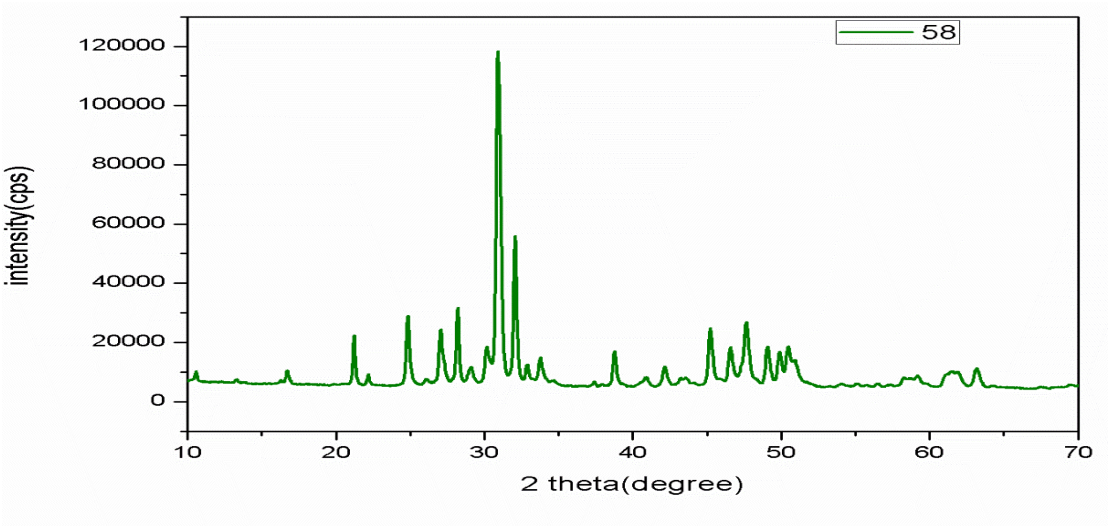


Fig. 6. XRD of $Sr_{1.75}Ca_{1.15}Dy_{0.05}Na_{0.05}(PO_4)_2$ prepared by Solid state method.

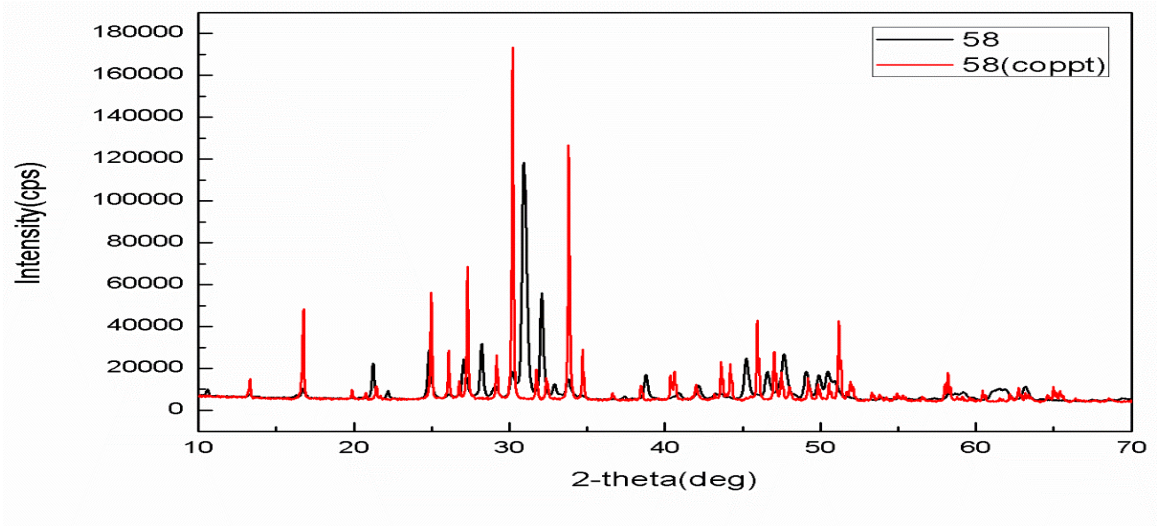


Fig. 7. XRD of $Sr_{1.75}Ca_{1.15}Dy_{0.05}Na_{0.05}(PO_4)_2$ prepared by solid state method as well as co-precipitation method at 1000 °C

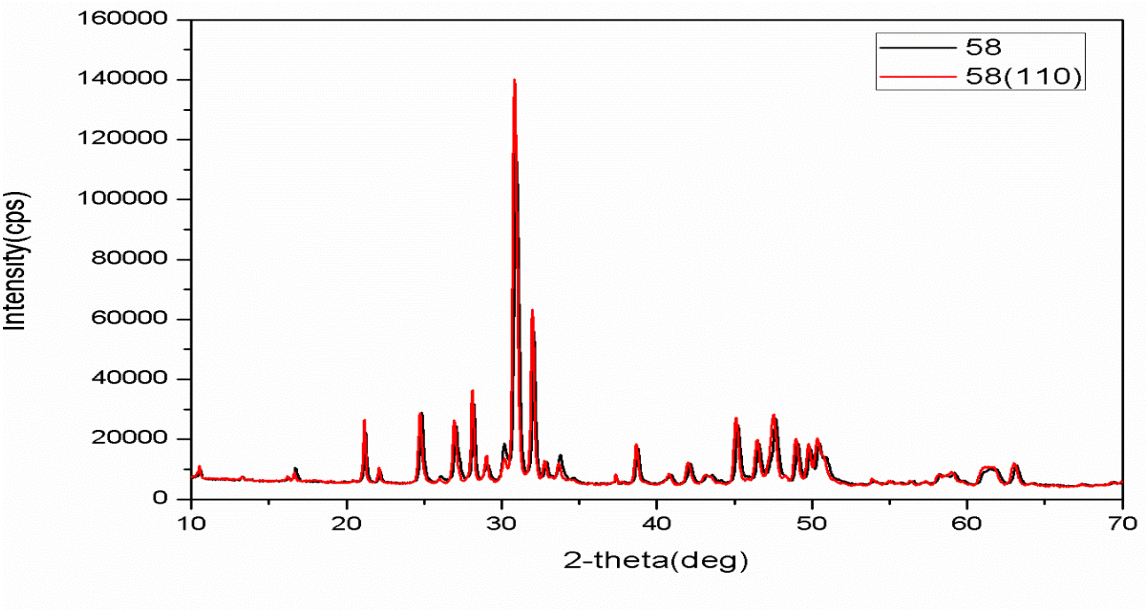


Fig. 8. XRD of $Sr_{1.75}Ca_{1.15}Dy_{0.05}Na_{0.05}(PO_4)_2$ prepared by solid state method as well as co-precipitation method at 1100° C.

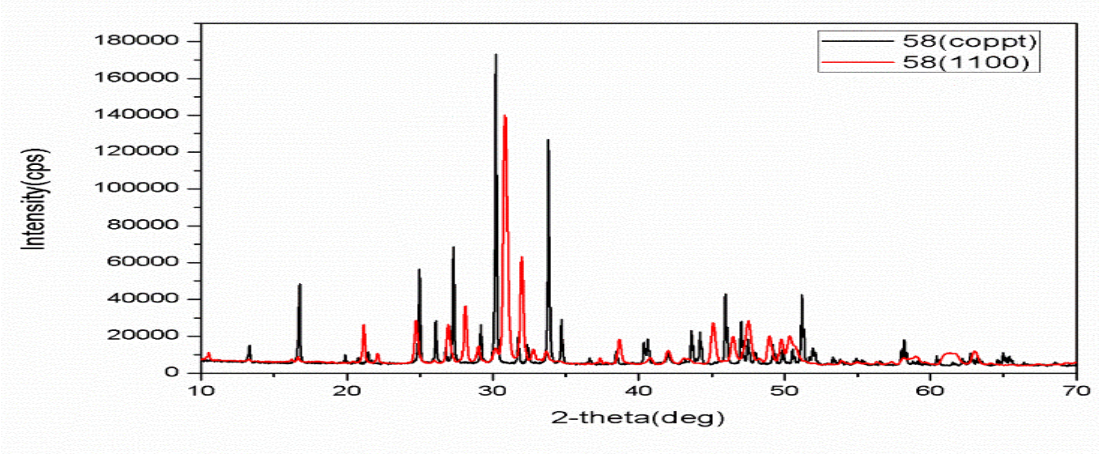


Fig.9. XRD of $Sr_{1.75}Ca_{1.15}Dy_{0.05}Na_{0.05}(PO_4)_2$ prepared by Co-precipitation method at 1000° C and 1100°C

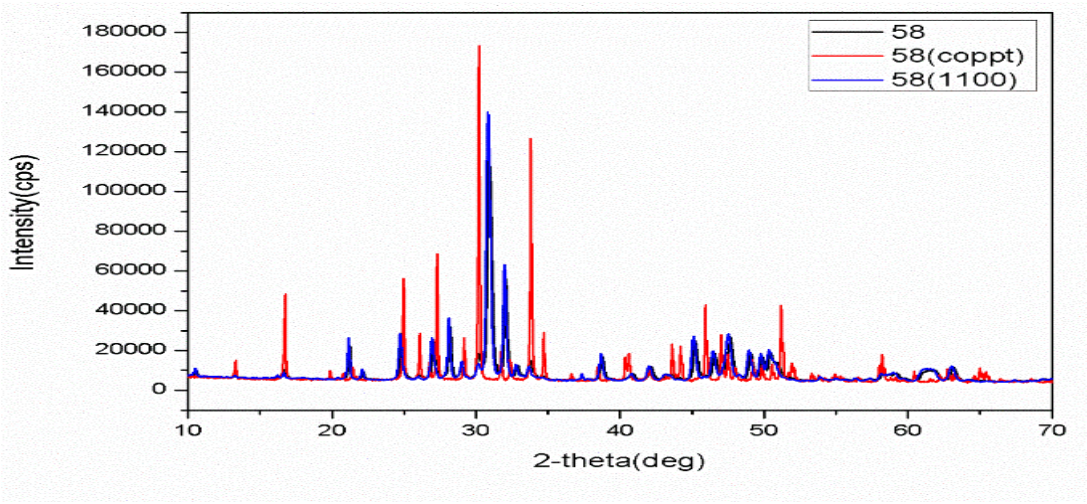


Fig 10. XRD of $Sr_{1.75}Ca_{1.15}Dy_{0.05}Na_{0.05}(PO_4)_2$ prepared by solid state method ,Co-precipitation method at 1000°C and 1100°C

3.8 DRS Spectra for Dy^{3+}

The DRS spectra of synthesized compounds $Sr_{1.75}Ca_{1.25}(PO_4)_2$ doped with various Dy^{3+} ion concentration are shown in fig. 11 and the data converted in to absorption and the same is shown in Fig.12. All the compositions show the characteristic absorption band of Dy^{3+} and are due to the f-f electronic transitions of Dy^{3+}.

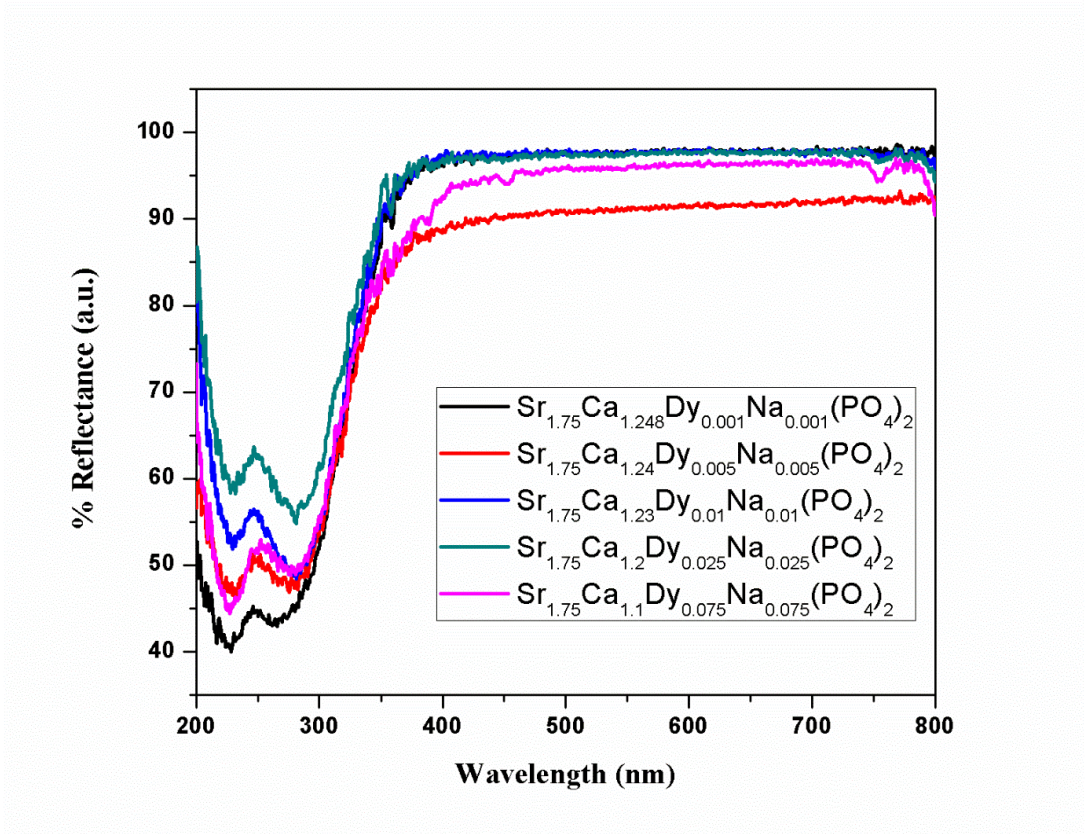


Fig.11. DRS spectra of $Sr_{1.75}Ca_{1.25}(PO_4)_2$ doped with various Dy^{3+}

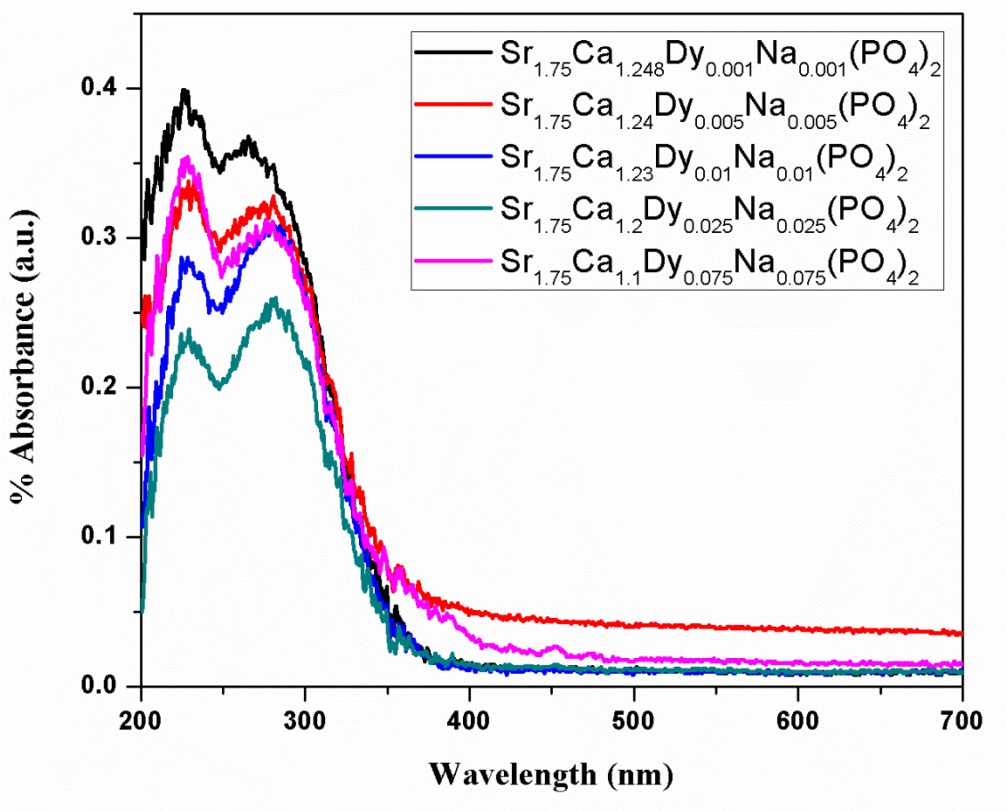


Fig.11. DRS spectra (% of Abs Vs wavelength (nm)) of $Sr_{1.75}Ca_{1.25}(PO_4)_2$ doped with various Dy^{3+}

3.9 Photoluminescence study of $Sr_{1.75}Ca_{1.25}(PO_4)_2$:*x*$Dy^{3+}$:

The photoluminescence emission spectrum is shown in Fig.12 and 13. Under monitoring at 575 nm corresponding to $^4F_{9/2}$–$^6H_{13/2}$ emission of Dy^{3+} ions, the spectra were made up of a series of bands. The peaks located at 323.2, 348.2, 362.6, 386.8, 424.2, 452.4 and 467.6 (472.6) nm belong to the intrinsic f–f transitions of Dy^{3+} from the ground state $^6H_{15/2}$ to the excited state $^4L_{19/2}$, $^6P_{7/2}$, $^6P_{5/2}$, $^4I_{13/2}$, $^4G_{11/2}$, $^4I_{15/2}$ and $^4F_{9/2}$, respectively. Of these excitation lines, the intensities of the 348.2, 362.6, 386.8 and 452.4 nm excitation peaks are much stronger than the others, which indicate that the compositions can be used for near-UV and blue LEDs based LEDs.

Fig. 14 and 15 shows the emission spectra of $Sr_{1.75}Ca_{1.25}(PO_4)_2$:*x*$Dy^{3+}$ phosphors excited by 348 nm and 387 nm UV light. It can be seen from the emission spectra that all the profiles of the emission spectra of $Sr_{1.75}Ca_{1.25}(PO_4)_2$:$Dy^{3+}$ are similar, and there are two dominating emissions at 481.6 (487) and 575 nm, corresponding to $^4F_{9/2}$–$^6H_{15/2}$, $^4F_{9/2}$–$^6H_{13/2}$ transitions, respectively. The $^4F_{9/2}$–$^6H_{13/2}$ transition belongs to a forced electric dipole transition, which is allowed only in the case that the Dy^{3+} ions are located at the local sites with non-inversion center symmetry. In $Sr_{1.75}Ca_{1.25}(PO_4)_2$:$Dy^{3+}$, from the emission spectra, the yellow emission

($^4F_{9/2}$–$^6H_{13/2}$) is stronger than the blue emission ($^4F_{9/2}$–$^6H_{15/2}$), indicating that Dy^{3+} is located in more non-centrosymmetric position in the $Sr_{1.75}Ca_{1.25}(PO_4)_2$ host lattice, which agrees with the conclusion of the structural analysis.

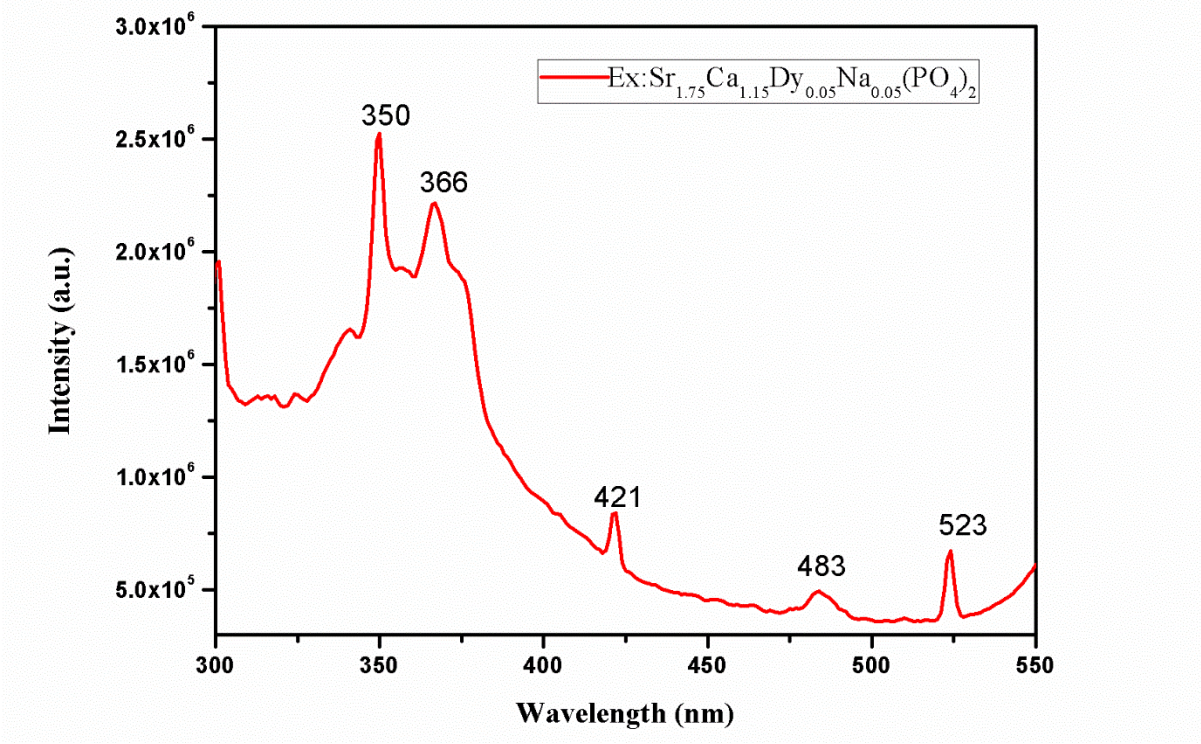


Fig. 12. The excitation spectrum of $Sr_{1.75}Ca_{1.15}Dy_{0.05}Na_{0.05}(PO_4)_2$

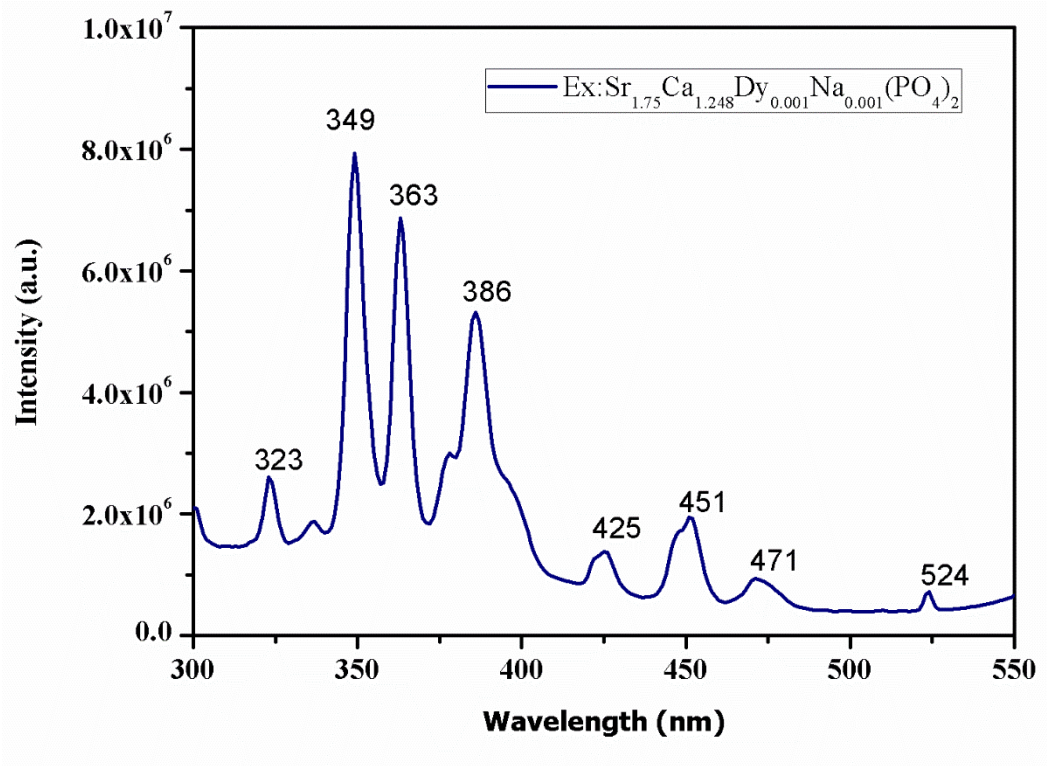


Fig. 13. The excitation spectrum of $Sr_{1.75}Ca_{1.248}Dy_{0.001}Na_{0.001}(PO_4)_2$

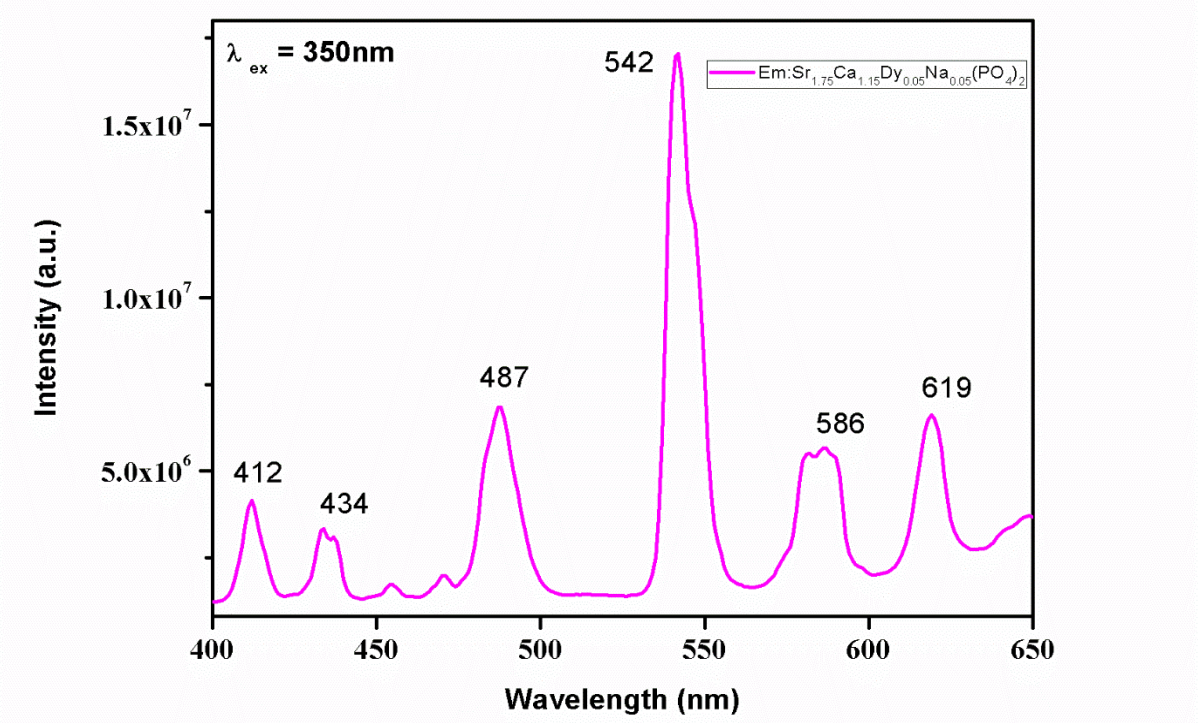


Fig. 14. The emission spectrum of $Sr_{1.75}Ca_{1.15}Dy_{0.05}Na_{0.05}(PO_4)_2$ under 350 nm excitation

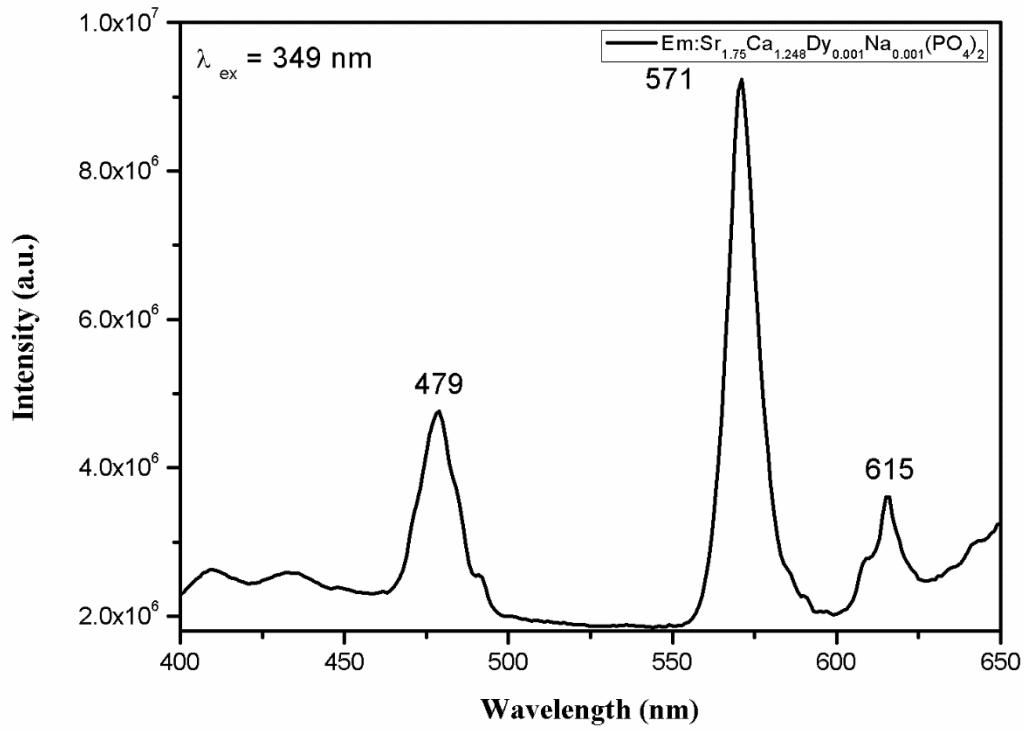


Fig. 15. The emission spectrum of $Sr_{1.75}Ca_{1.15}Dy_{0.05}Na_{0.05}(PO_4)_2$ under 350 nm excitation

3.10 Colour chromaticity coordinates CIE diagram:

The colour chromaticity coordinates was calculated by using emission spectral data (Fig. 16). The data which is obtained clearly indicates with different concentration of Dy showing range of colours, starting from organish-yellow to white [Dy0.05 (x = 0.5768, y = 0.3596), Dy0.01 (0.3230, 0.3537) and Dy0.025 (0.3925, 0.4159)].

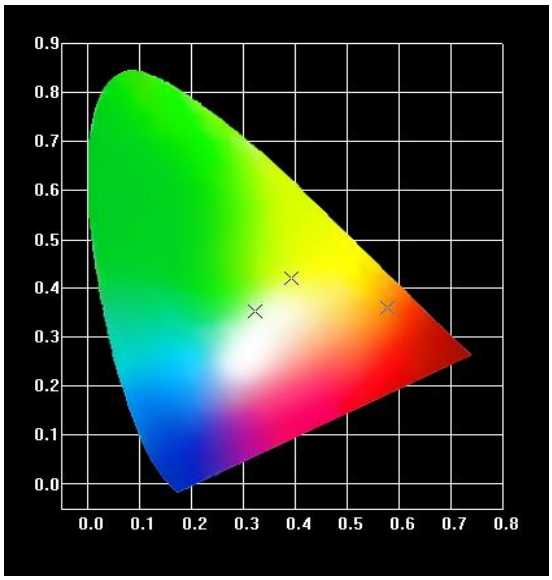


Fig. 16. The CIE diagram of $Sr_{1.75}Ca_{1.25}(PO_4)_2:Dy^{3+}$

Composition	**X**	**Y**
$Sr_{1.75}Ca_{1.2485}Dy_{0.001}Na_{0.001}(PO_4)_2$	**0.5768**	**0.3596**
$Sr_{1.75}Ca_{1.23}Dy_{0.01}Na_{0.01}(PO_4)_2$	**0.3230**	**0.3537**
$Sr_{1.75}Ca_{1.2}Dy_{0.025}Na_{0.025}(PO_4)_2$	**0.3925**	**0.4159**

3.11 Image of Dy^{3+} under UV lamp

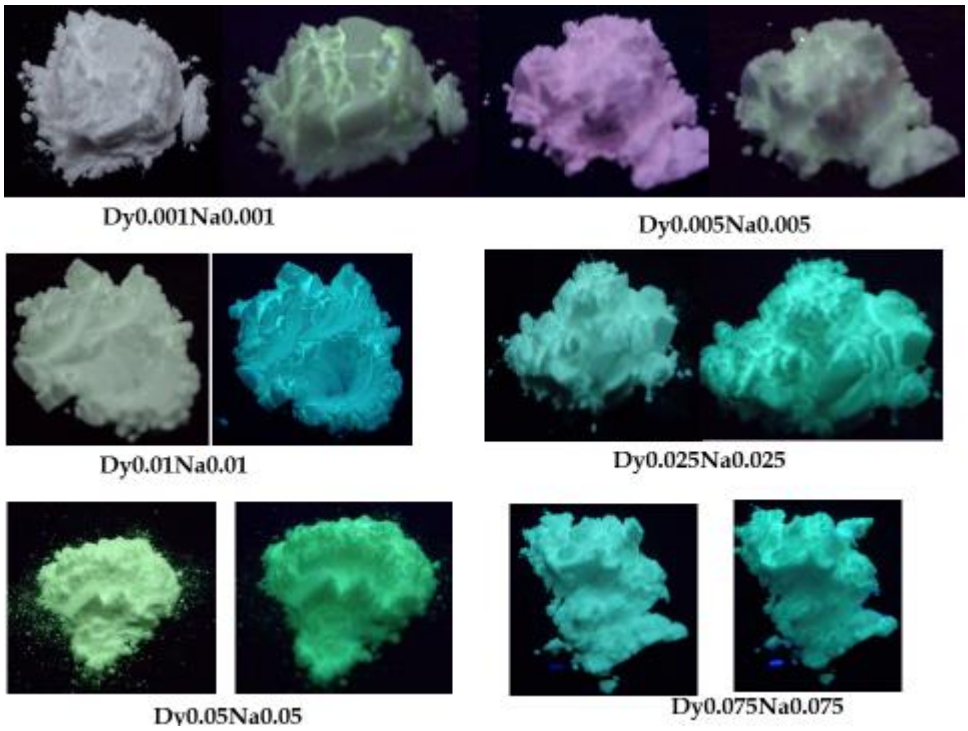


Fig. 17. Images of Dy^{3+} doped $Sr_{1.75}Ca_{1.25}(PO_4)_2$ at different concentrations

Summary and Conclusion:

In the present investigation, dysprosium doped $Sr_{1.75}Ca_{1.25}(PO_4)_2$ were prepared in different stoichiometry using solid state synthesis and co-precipitation technique. DRS and XRD studies were carried out for the above prepared compounds and the characterization results were found to be similar through both the methods. The calculated CIE values are clearly indicates with different concentration of Dy showing range of colours, starting from organish-yellow to white.

The Eu^{3+} doped host lattice $La_{0.95}Eu_{0.05}BW_{1-x}Mo_xO_6$ was synthesized by conventional high temperature solid-state reaction. All the compositions show red emission, however the emission various with different Mo concentration. $La_{0.95}Eu_{0.05}BW_{0.8}Mo_{0.2}O_6$ shows intense red emission and which clearly indicates that the appropriate W and Mo concentration is necessary to obtain Eu^{3+} red emission and shows the CIE chromaticity coordinate values x = 0.6647 and y = 0.3349, which were close to the National Television Standard Committee (NTSC) standard values. Based on the spectral studies one can conclude that the presently synthesised may find potential applications in the white LED based on yellow + red phosphor.

Future perspective:

Explore the other host lattice for the Dy^{3+} activation and generate the white light emission

The concentration variation to be carried out in order to study the structure-compositions-property- correlations

Further other mixed metal oxides systems also be explored to generate red emission by Eu activation and the concentration to be varied to generate high emission intensity

The synthesised phosphor to be incorporated in the white LEDs.

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